

The Effectiveness of Active Carbon Adsorbent of Cassava Peel (Manihot Esculenta Cranzts) in Reduce Level of Chromium Metal in Tannery Liquid Waste

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ABSTRACT

This study aims to determine the characteristics, the effect of mass variation, the percentage of adsorption effectiveness of cassava peel activated carbon activated with 0.5 M HCl and activated with 0.5 M H₂SO₄ on the adsorption of Cr metal in leather tanning wastewater and its morphology. The subject of this research is the adsorbent of cassava peel before it is activated, activated by chloric acid 0,5 M, and activated by sulfuric acid 0.5 M. meanwhile the object of this research is the effectiveness of cassava peel adsorbent in reducing chromium metal content in tannery liquid waste. Cassava peel was carbonized at 500 °C for 1 hour. The cassava peel carbon was characterized according to SNI 06-3730-1995. The adsorption process is performed by batch method. Analysis was performed by Atomic Adsorption Spectrophotometer, PSA, and SEM-EDX. The result of the characterization of cassava peel carbon showed that the moisture content, ash content, adsorption capacity of 12 met SNI, meanwhile the carbon content and volatile matter content did not meet SNI. The adsorption efficiency of chromium metal is 95.97% for carbon before activated, 95,33% for carbon activated by chloric acid, and 96.65% for carbon activated by sulfuric acid. The result of PSA size of cassava peel adsorbent before activated by chloric acid and sulfuric acid were 34.484 μm, 42.504 μm, and 37.059 μm respectively. Cassava peel adsorbent has a Langmuir adsorption type. The SEM-EDX result showed that the adsorbent from cassava peel had a dissimilar pore shape.

Keyword: carbon, cassava peel, adsorption, tannery liquid waste, chromium

1. INTRODUCTION

As one of the developing countries, industries in Indonesia are starting to emerge and are producing people's needs. With the increasing number of industries, it is undeniable that many production by-products are also produced as waste. One of them is heavy metal waste. Heavy metals contained if they exceed the threshold will cause serious environmental contamination and also have dangerous toxic properties that can cause serious illness if they enter the human body (Danarto, 2007), such as leather tanning industry. The processing of leather products, although it provides a large added value to raw hides, also has the potential to cause pollution to the environment due to the use of certain chemicals in the process which are potentially harmful to the environment (Luqman et al, 2016). The liquid waste generated from the leather tanning process still contains chromium in a large enough

concentration so that it would be dangerous if disposed of directly without being treated first. Chromium (Cr) is the most widely used leather tanning agent by the leather tanning industry and around 85% of the world's tanned leather uses chromium (Barcodit et al., 2014). Leather tanned using chromium has several advantages, including having high tensile strength, being more flexible, being more resistant to high temperatures, and giving good results in painting (Mustakim M et al, 2010).

Hexavalent chromium (Cr^{6+}) from leather tanning industry waste is usually present in the form of chromate (CrO_4^{2-}). The toxicity of chromium metal depends on the valence of the chromium element, and the toxicity of chromium (VI) is a hundred times that of chromium (III) (Perdana, M, 2013). The heavy metal chromium can cause lung cancer, liver and kidney damage. If in contact with the skin it can cause irritation even in high concentrations it can cause skin cancer and if swallowed it can cause abdominal pain, vomiting, and at high concentrations it can cause cancer of the digestive tract (Tjokrokusumo, 1999). One of the ways used to handle industrial waste such as chemical waste contained in the waste stream is the principle of separation. The way that is more often used on the principle of separation is the adsorption method (Wijayanti, 2009).

Additionally, the based carbon to the activated process is low cost but effective in producing a material that are easy to regenerate and selective to adsorb heavy metals (Wan Ngah W S and Hanafiah, 2008). Adsorption is a process of adsorbing atoms, ions or molecules in solution on an absorbent surface. This process occurs on the surface of a two-phase substance, namely between the gas-solid phase or the liquid-solid phase. Substances that are absorbed in the adsorption process are called adsorbates, while substances that absorb are called adsorbents (Saputri, 2020).

The use of biomaterials as heavy metal ion adsorbing agents is an alternative that is often used. Biological material is one of the adsorbents with good prospects. (Wijayanti, 2009). One of the interesting organic wastes is cassava peel. Cassava peel contains high carbohydrates, indicating that the material also contains a high carbon element (Utomo et al., 2014). The high carbon content in cassava peel has the potential to be processed into an adsorbent in the form of activated carbon which has added value and wider utilization. Adsorbents can be used for industrial wastewater treatment. In addition, the use of cassava peels as an adsorbent is also an effort to reduce solid waste in the cassava processing industry (Saillah, I, dkk, 2020).

Cassava peel is one of the biomass materials that has not been widely used and has the potential as an adsorbent for heavy metals. The content of non-reducing cellulose in cassava peel can effectively bind metal ions. So far, cassava peel waste has not been utilized optimally, even though cassava peel waste can be used as raw material for activated carbon. The dried cassava peel is then carbonized and activated using hydrochloric acid and sulfuric acid. Carbon is then characterized according to SNI 06-3730-1995. The instruments used are atomic absorption spectroscopy (AAS), scanning electron microscope-energy dispersive x-ray (SEM-EDX) and particle size analyzer (PSA). Based on this description, it is necessary to conduct research to reduce problems regarding leather tanning waste. This was done with the intention of overcoming this problem by looking for the effectiveness of the adsorbent, namely activated carbon of cassava peels, to adsorb Cr (chromium) metal in leather tanning waste.

2. RESEARCH METHOD

2.1. Chemicals

The materials required are Cassava peel, tannery liquid waste, HCl (pa E Merck), H_2SO_4 (pa E Merck), Iodine solution (pa E Merck), $\text{Na}_2\text{S}_2\text{O}_3$ (pa E Merck), amylum, aquadest.

2.2. Instruments

The tools used are the Atomic Absorption Spectrophotometer type AA-7000 Shimadzu, SEM-EDX JEOL JED-2300, Laser Particle Sizer Testing LLPA-C10 PSA, magnetic stirrer plus electric heater, oven, vacuum pump, hot plate, analytical balance, pH meter, shaker, 100 mesh sieve, mortar and pestle, and glassware. aluminium foil.

2.3. Activated Carbon Preparation

Cassava peel is washed, cut into small pieces, then dried in the sun to dry. After drying, the skin is roasted. Cassava peel is carbonized by putting it in the furnace for 1 hour at 500 °C. After that, the cassava skin was pounded and sieved using a 100 mesh sieve. Furthermore, cassava peel carbon is soaked using 0.5 M hydrochloric acid solution and 0.5 M sulfuric acid solution for 24 hours. Then the carbon is filtered and rinsed using distilled water until a neutral pH is obtained. After that, the carbon was dried in an oven at 110°C for 3 hours.

2.4. Carbon Application

A total of 50 ml of leather tanning waste samples were put in erlenmeyer then given a magnetic stirrer. Then put it on the hot plate. Cassava skin carbon is then added with a mass variation of 0.5; 1.0 and 2.0 grams into the erlenmeyer containing the sample. The sample and carbon mixture was stirred for 90 minutes for each mass variation. After that the mixture is then filtered using filter paper. Repeat these steps for carbon activated with 0.5 M hydrochloric acid and activated with 0.5 M sulfuric acid. Repeat these steps for carbon activated with 0.5 M hydrochloric acid and activated with 0.5 M sulfuric acid.

2.5. Characterization of Carbon

Cassava peel carbon is characterized according to SNI 06-3730-1995 which includes water content, ash content, volatile matter (volatile), carbon content and adsorption capacity of I2. Then it was analyzed using a Particle Size Analyzer (PSA) to determine particle size and SEM-EDX to determine the morphology of carbon. The content of chromium metal in leather tanning waste was analyzed using an atomic absorption spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Characterization of Carbon Cassave Peel

In this study, cassava peel adsorbents were prepared through several processes. The process begins with dehydration of cassava skin carbon until the cassava skin is dry. After that, the cassava peel was carbonized at 500 °C for 1 hour until charcoal was formed. Then pulverized by mashing and sifting with a size of 100 mesh to obtain particles with a uniform size. After that, the carbon was activated using 0.5 M hydrochloric acid solution and also 0.5 M sulfuric acid solution by soaking for 24 hours then filtered and neutralized with distilled water. According to Fitri Wulandari (2014) activation has the goal of opening or creating pores so that adsorbate can pass through, increasing the distribution and pore size and expanding the surface area of activated carbon. Neutralization using distilled water while washing the carbon to remove impurities in the adsorbent.

Tabel 1. Carbon Characterization of Cassava Peel

Types of Carbon	Water content (%)	Ash content (%)	Volatile content (%)	Carbon content (%)	Adsorption to Iodium (mg/g)
Carbon Before Activation	0,48	7,00	34,85	57,67	6014,13
HCl Activated Carbon	1,22	8,36	33,94	64,18	6079,99
H ₂ SO ₄ Activated Carbon	1,67	4,48	32,77	63,16	6116,04
SNI No. 06-3730-1995	Maks. 15	Maks. 10	Maks. 25	Min. 65	Min. 750

Based on the results of characterization tests, on water content, volatile matter content, and carbon content, unactivated carbon had better results. At ash content, sulfuric acid activated carbon has better results. The adsorption power of iodine, sulfuric acid activated carbon has a higher yield. According to SNI 06-3730-1995, the moisture content has a maximum value of 15%, the ash content has a maximum value of 10%, the volatile matter content has a maximum value of 25%, the minimum carbon content is 65%, and the adsorption capacity of iodine is with a minimum value of 750 mg /g. The resulting cassava peel carbon has yields that almost comply with SNI 06-3730-1995 at carbon content of 64.18% (activated HCl) and 63.16% (activated H₂SO₄). According to SNI 06-3730-1995 at a minimum carbon content of 65%, so the results of this study are close to SNI. The level of volatile matter produced exceeds the threshold of the SNI value. This is because the carbonization process that occurs is not perfect. When activated carbon uses chemicals, oxidation will occur which can damage the inside of the activated carbon so that the pores become larger (Rohmah & Redjeki, 2014).

The cassava peel adsorbent was then analyzed using PSA to determine particle size. PSA results show that the particle size of the carbon before activation has a size of 34.484 μm. Whereas HCl activated carbon has a particle size of 42,504 μm and H₂SO₄ activated carbon has a particle size of 37,059 μm. From the data obtained, the particle size of the carbon before activation has the smallest particle size compared to activated carbon. This affects the adsorption power of carbon. Activated carbon can adsorb certain gases and chemical compounds or its adsorption properties are selective, depending on the size or volume of the pores and surface area. This pore structure is closely related to carbon absorption, where there are more pores on the surface of activated carbon, the adsorption capacity also increases (Landiani, 2016). Particles that have a small size have a large surface area, so they have better adsorption power. The particle size of the carbon before and after activation was analyzed using a particle size analyzer instrument. The results of the analysis are shown in Figure 1.

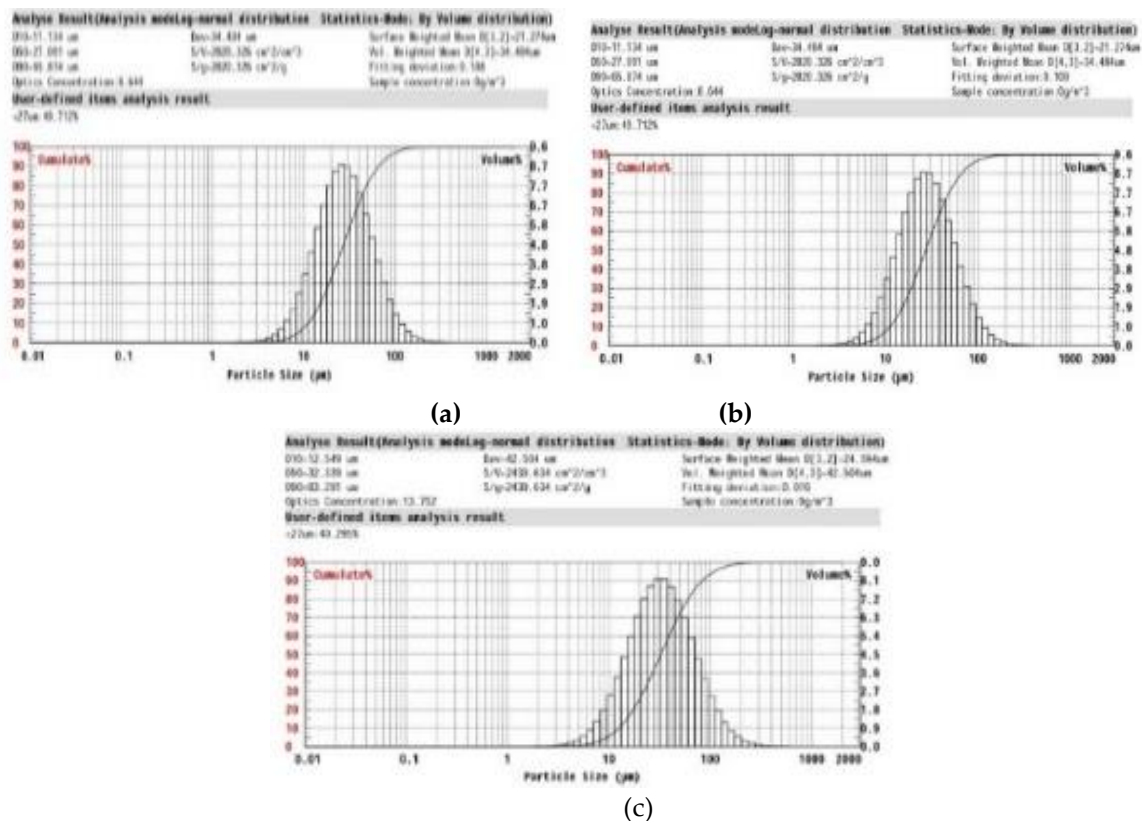


Figure 1. PSA results of cassava peel carbon (a) without activation (b) activated by HCl (c) activated by H₂SO₄

Surface morphology of activated charcoal adsorbent on cassava peel activated carbon used in the adsorption process was then tested using EDX. The SEM-EDX results yield some data such as topography and composition of the samples being analyzed. There are two SEM-EDX analyzes carried out in this study, namely on the initial adsorbent and on the adsorbent that has been used in the adsorption of leather tanning waste shown in Figures 2 and 3.

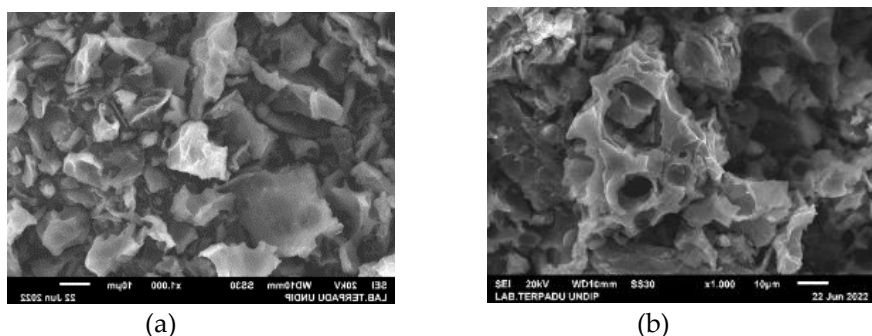


Figure 2. SEM results of Cassava Peel Carbon at 1000 x magnification, before adsorption Cr (a) after adsorption Cr (b)

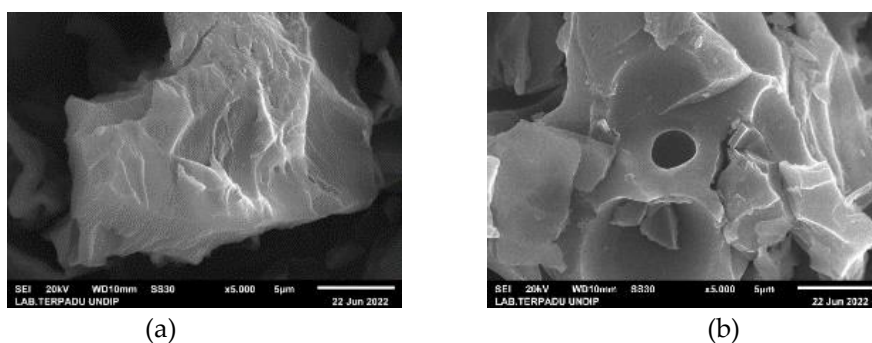


Figure 3. SEM results of Cassava Peel Carbon at 5000 x magnification, before adsorption Cr (a) after adsorption Cr (b)

Based on Figures 2 and 3, it can be seen the difference in surface morphology of activated carbon before and after activation. On cassava peel activated carbon which had been activated using 0.5 M H_2SO_4 , it was seen that the distribution of pores was more regular with a higher number of pores than before activation. This is due to activation using sulfuric acid which is able to dissolve impurities so that there are more pores. In addition, it can be seen that the pore size in activated carbon after activation is larger than before activation. The large number of pores and the width will increase the surface area of activated carbon. The greater the surface area of activated charcoal, the greater the adsorption capacity and rate (Adamson, 1990). Activated carbon after activation has the maximum adsorption capacity of the adsorbate compared to activated carbon before activation.

Based on Figures 2 and 3 it shows that cassava peel carbon has a non-uniform pore shape. Based on the results of the EDX analysis contained in Figure 4(a), it is known that Cr metal appears on the graph but in the graph of the content of Cr metal is not detected. This is because the concentration of Cr metal that was read did not exceed the detection limit of the SEM-EDX tool.

The carbon structure before being applied to adsorb contained C, O, Ca, and Cu with each percentage (% by mass) namely C of 79.12%, elemental O of 20.30%, elemental Ca of 0.14% and elemental Cu of 0.45%. The content in the form of oxide on the first adsorbent is C, CaO, and CuO. The

results of the SEM-EDX analysis of cassava peels after adsorption are shown in Figure 4(b). The results of the EDX analysis showed that the carbon structure of cassava peel after adsorption contained the elemental composition of C, O, Na, Cl, Ca, Cr, and Cu with each percentage (% by mass), namely C of 78.71%, element O of 19.75%, element 0.40% Na, 0.23% Cl, 0.33% Ca and 0.58% Cu. The content in the form of oxide on the first adsorbent is C, NaO, Cl, CaO and CuO. From the analysis of cassava peel carbon with EDX, there are differences in the elemental composition contained in the carbon before adsorption and the carbon after adsorption. The difference is the appearance of the elements Cl, Cr, and Na. these elements arise due to the activation of activated carbon using an activator and also from leather tanning waste.

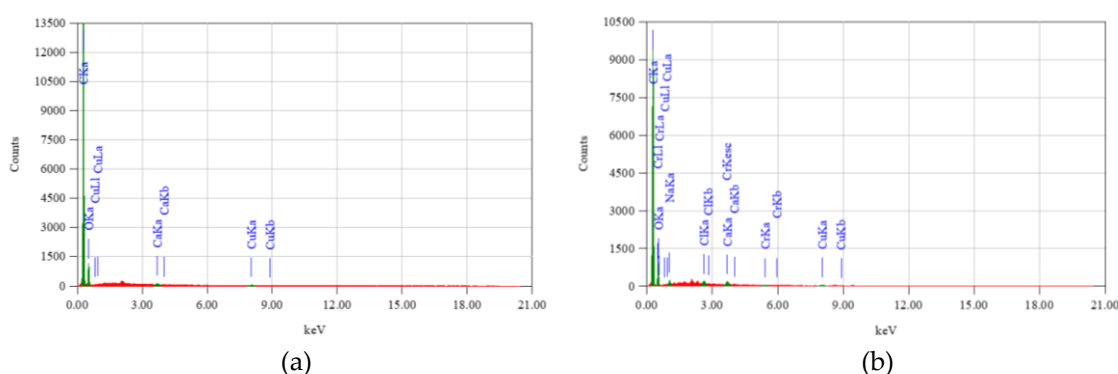


Figure 4. EDX spectrum of activated carbon before adsorption Cr (a) after adsorption Cr (b)

3.2. Application of Cassava Peel Activated Carbon

The content of Cr metal in leather tanning waste based on the results of the AAS test is shown in Tables 2, 3 and 4. Adsorption using activated carbon was carried out using 3 mass variations of cassava skin activated carbon. The experiment was carried out with three repetitions. The adsorption process of chromium metal in leather tanning waste was carried out using a batch method. The carbon used in this adsorption process is carbon before activation and carbon after activation. After the adsorption process, the metal content was analyzed again using the AAS instrument. The decrease in the concentration of Cr metal in each type of carbon decreased significantly in the mass variation 2 grams. For carbon before activation has a decrease of 107.40 mg/L with an efficiency of 95.97%. For hydrochloric acid activated carbon has a decrease of 105.67 mg/L with an efficiency of 95.33%. Sulfuric acid activated carbon has a reduction of 107.14 mg/L with an efficiency of 96.65%. This shows that the more carbon mass used, the greater the adsorption efficiency. Carbon before activation showed the best results in the adsorption of Cr metal in leather tanning waste. Based on these data it can be before activation and after activation are effective in adsorbing Cr metal in leather tanning waste.

Table 2. Unactivated Carbon Adsorption

Mass Variation (g)	Initial Concentration (mg/L)	Final Concentration (mg/L)	Ea (%)
0,5	110,86	4,36	96,06
1,0	110,86	4,74	95,72
2.0	110,86	4,46	95,97

Table 3. Carbon Adsorption Efficiency Data

Mass Variation (g)	Initial Concentration (mg/L)	Final Concentration (mg/L)	Ea (%)
0,5	110,86	5,60	94,96
1,0	110,86	5,49	95,05
2.0	110,86	5,18	95,33

Table 4. H₂SO₄ Activated Carbon Adsorption Efficiency Data

Mass Variation (g)	Initial Concentration (mg/L)	Final Concentration (mg/L)	Ea (%)
0,5	110,86	4,79	95,68
1,0	110,86	4,12	96,28
2,0	110,86	3,72	96,65

3.3. Adsorption Isotherm

The isotherm curve is obtained from the calculation of the concentration of chromium metal which is analyzed using AAS. The isotherm curves are shown in Figures 5, 6 and 7.

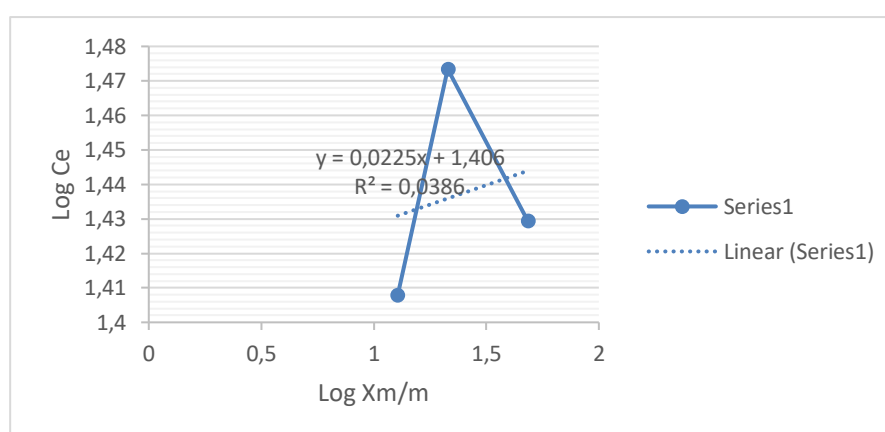


Figure 5(a). Freundlich Isotherm Curve Carbon Before Activation

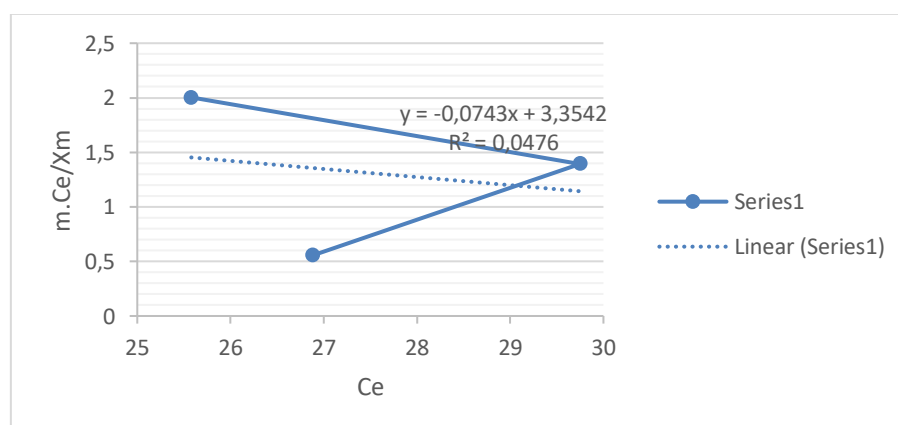


Figure 5 (b) Langmuir Isotherm Curve Carbon Before Activation

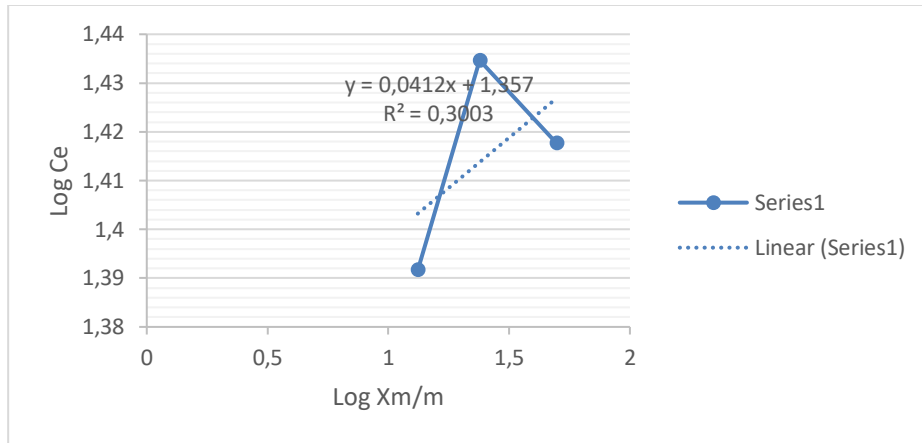


Figure 6(a). Freundlich Isotherm Curve HCl Activated Carbon

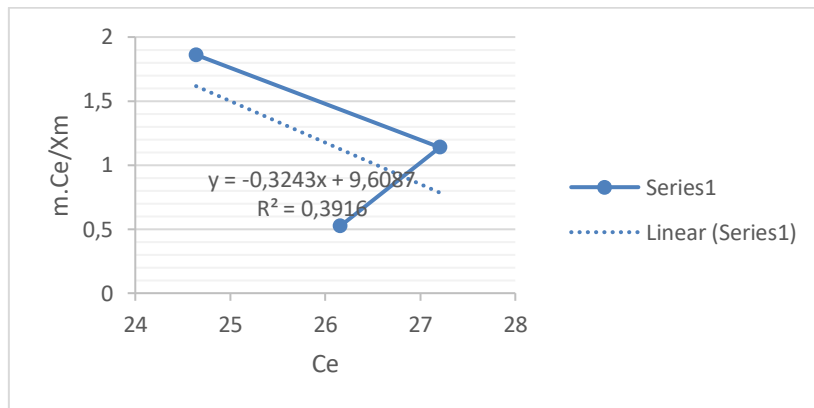


Figure 6 (b). Langmuir Isotherm Curve HCl Activated Carbon

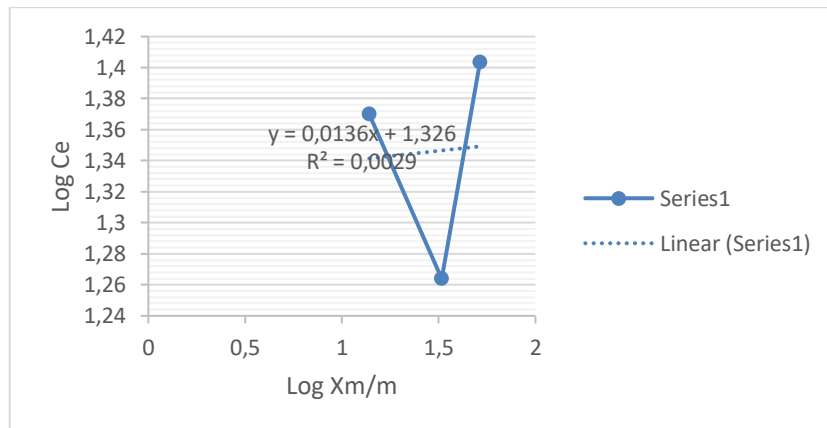


Figure 7(a). Freundlich Isotherm Curve Activated Carbon H₂SO₄

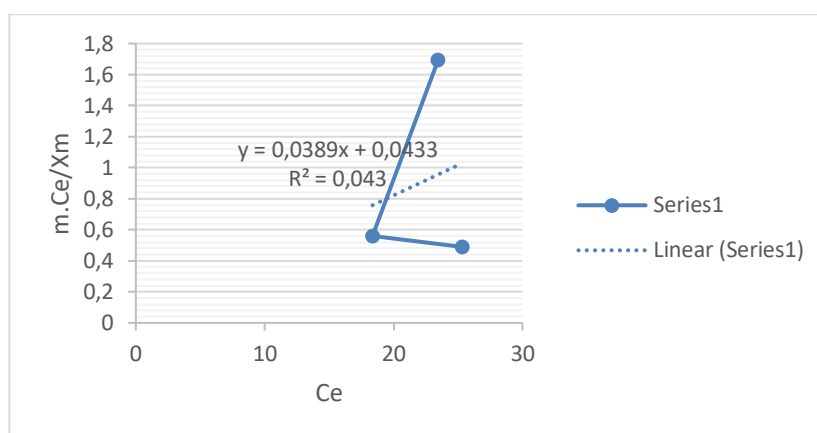


Figure 7(b). Langmuir isotherm curve Activated Carbon H₂SO₄

The adsorption process by an adsorbent is influenced by several factors and has a specific adsorption isotherm pattern. The type of adsorbent, the type of substance adsorbed, the surface area of the adsorbent, the concentration of the adsorbed substance, and temperature are some of the factors that affect the adsorption process. With these factors, each adsorbent that absorbs one substance with another substance will not have the same adsorption pattern. It is known that there are two types of adsorption isotherm pattern equations commonly used in adsorption processes in solution, namely the Langmuir and Freundlich adsorption equations (Imas, 2019).

Testing this balance model is used to determine the most appropriate model in this study. The determination of the adsorption isotherm involves solving the Langmuir equation which is converted into a straight line equilibrium curve. Furthermore, the determination of the equilibrium model is seen at the highest value of the determinant coefficient (R^2). The type of adsorption isotherm is determined by the condition where the largest adsorption process occurs. Determination of the type of adsorption is determined based on the value of the correlation coefficient (R^2) shown by the graph of the linear equation of each isotherm curve. The Freundlich and Langmuir isotherm equations are determined by first calculating X_m/m , $C_e/(X_m/m)$, $\log C_e$ and $\log X_m/m$. The Freundlich adsorption type was determined using the relationship between $\log X_m/m$ and $\log C_e$, while the Langmuir adsorption type used the relationship between C_e and $m.Ce/X_m$. Adsorption with a linear equation which has a correlation coefficient value (R^2) close to 1, it can be concluded that the adsorption isotherm follows this equation (Pranoto, 2020).

Based on the results, the R^2 value of the equation does not fulfill the adsorption isotherm for either the Freundlich isotherm or the Langmuir isotherm. The three adsorbents have different values between the two isotherms. The R^2 value on the Langmuir isotherm is much larger than the Freundlich isotherm, so the adsorption type for the three types of carbon tends to belong to the Langmuir isotherm. The Langmuir adsorption process showed that the surface interaction of the adsorbent with the adsorbed substance, namely Cr metal, was limited to the formation of a monolayer. According to Pranoto (2020), this Langmuir isotherm shows that the adsorption process between the adsorbent and the adsorbate occurs chemically, that is, on the surface of the adsorbent there are homogeneous active sites which will interact with metal ions by forming a compound.

4. CONCLUSION

Based on the results of the discussion, it can be concluded that the characterization results of cassava peel carbon before activation have a better value than carbon after activation. Characterization of carbon before and after activation complies with SNI 06-3730-1995 except for the value of volatile matter and carbon content. The adsorption type for the three adsorbents, namely Langmuir, with adsorption describing the formation of a monolayer. Cassava peel adsorbent has a non-uniform surface

morphology. There are several differences in the elements in the adsorbent before and after adsorption. The adsorption efficiency of cassava peel carbon on adsorption of chromium metal in tannery liquid waste was 95.97% non-activated carbon, 95.33% hydrochloric acid activated carbon, and 96.65% sulfuric acid activated carbon.

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